Science Advances
AAAS
advances.sciencemag.org/cgi/content/full/4/4/eaao7265/DC1

Supplementary Materials for

Geoelectrochemical CO production: Implications for the autotrophic origin of life

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Published 4 April 2018, *Sci. Adv.* **4**, eaao7265 (2018)
DOI: 10.1126/sciadv.aao7265

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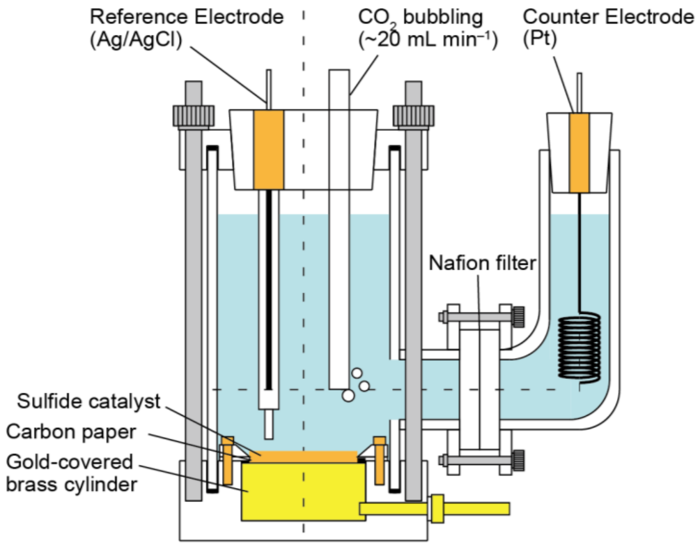

fig. S1. A schematic of the electrochemical cell. The cell is made of a Pyrex glass tube sandwiched between a polyoxymethylene (POM) cap and basement that were tightened together with stainless screws and knurled nuts. The cell has two compartments: a large working electrode side (~100 mL) and a small counter electrode side (~15 mL) that are separated by a proton exchange membrane (Nafion 117; DuPont). On the working electrode side, a gold-coated brass cylinder is placed at the center of the POM basement, and is coated with carbon paper (5.7 cm^2) with a silicon and POM packings. An Ag/AgCl electrode (in saturated KCl) is used as the reference, and is fixed at a distance of less than 0.5 cm from the working electrode to reduce solution resistance. On the counter side, a platinum coil is inserted into the glass tube, and is used as the counter electrode

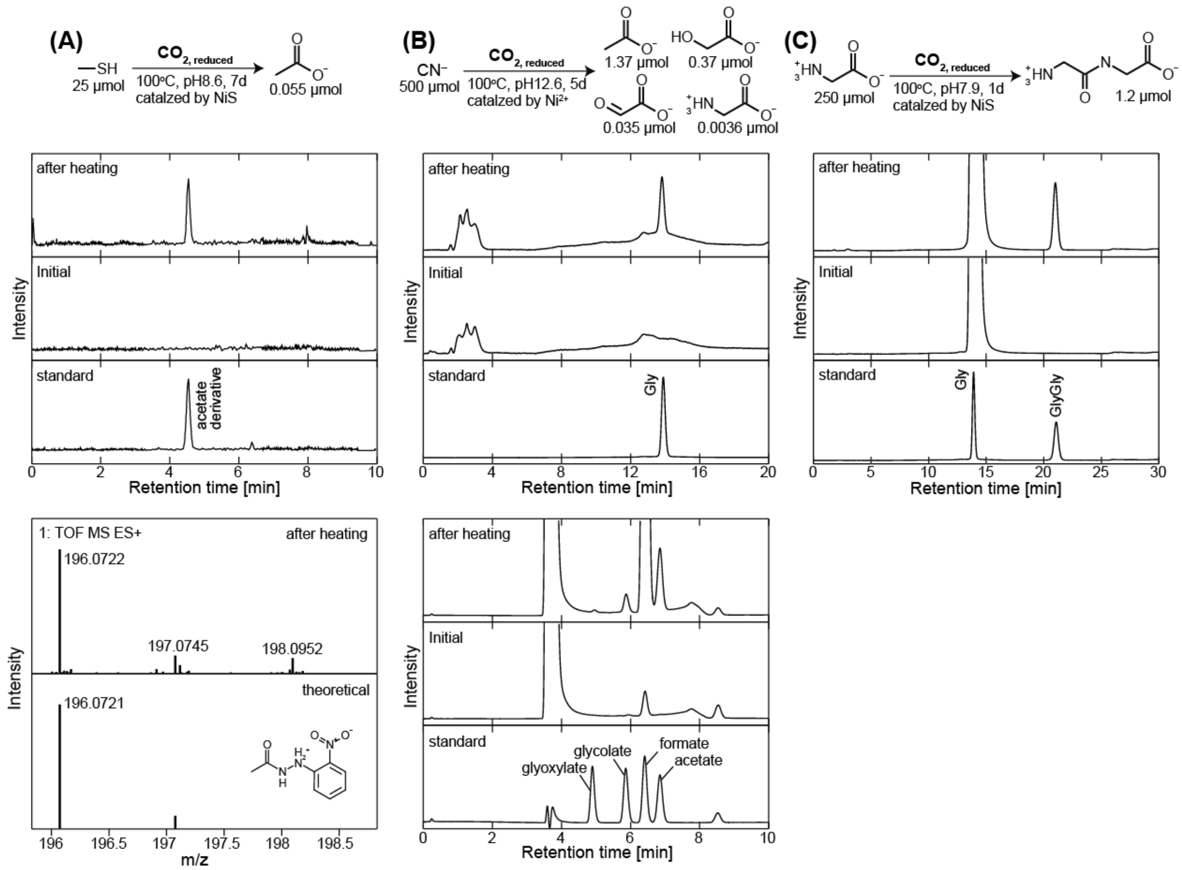

fig. S2. Abiotic organic synthesis driven by the electrochemically generated reductive gas on CdS at –1.0 V (versus SHE) in 100 mM NaCl saturated with 1 atm of CO_2. The product chromatograms are shown together with those of the standards and initial samples. **(A)** Extracted ion chromatograms at the m/z between 196.047 and 196.111 (top) and mass spectrum at 4.55 min for the heated sample (bottom). **(B)** Chromatograms for glycine (top) and organic acids (bottom). **(C)** Chromatograms for glycine and glycylglycine.

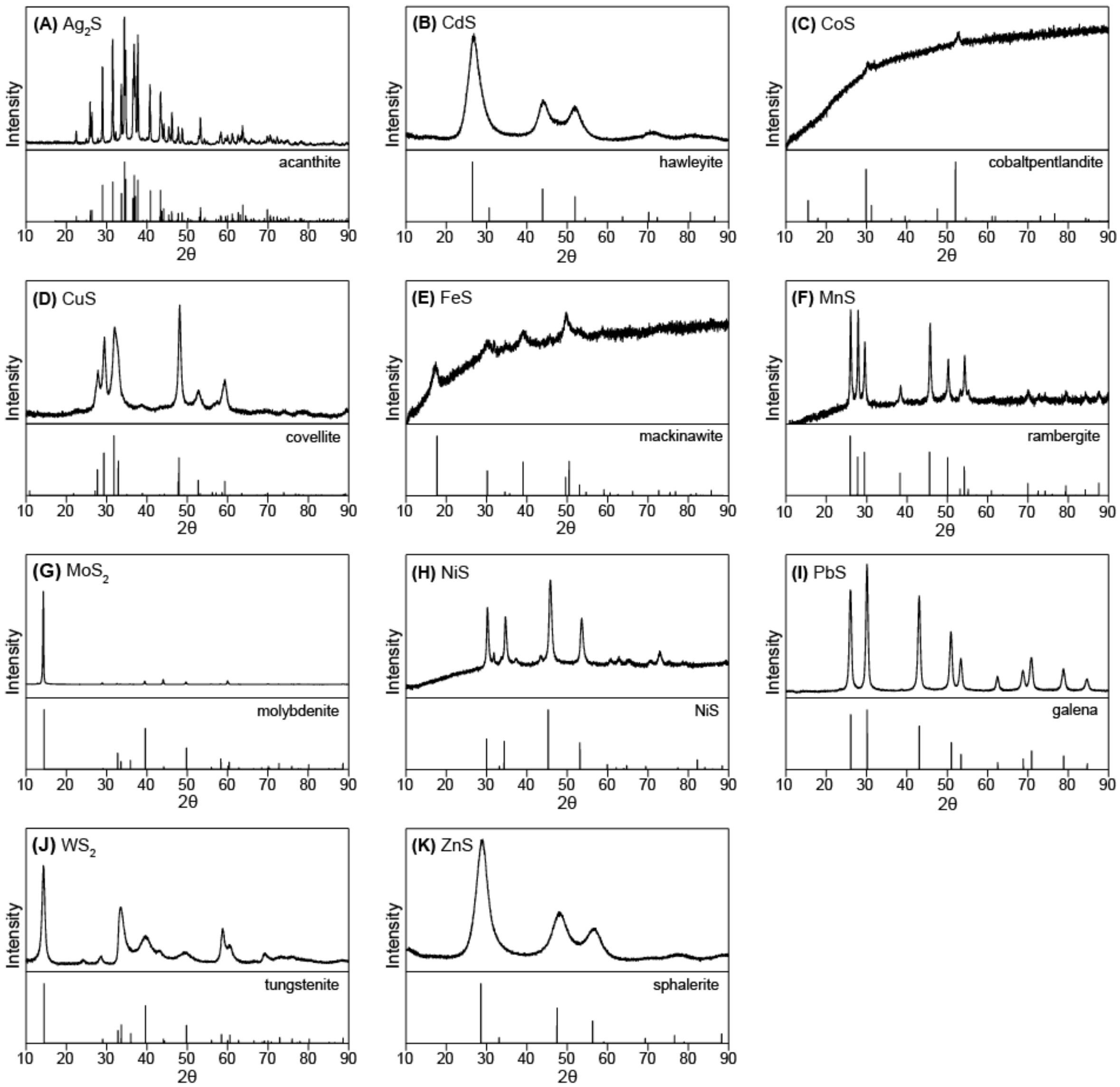

fig. S3. X-ray diffraction patterns of metal sulfides. All runs were conducted with 2θ ranging from 10º to 90º using 0.02º 2θ step with a scan rate of 1º min^{-1}. Reference patterns were taken from the PDF (Power Diffraction File) published by the International Centre for Diffraction Data. See table S2 for the peak positions and assignments.

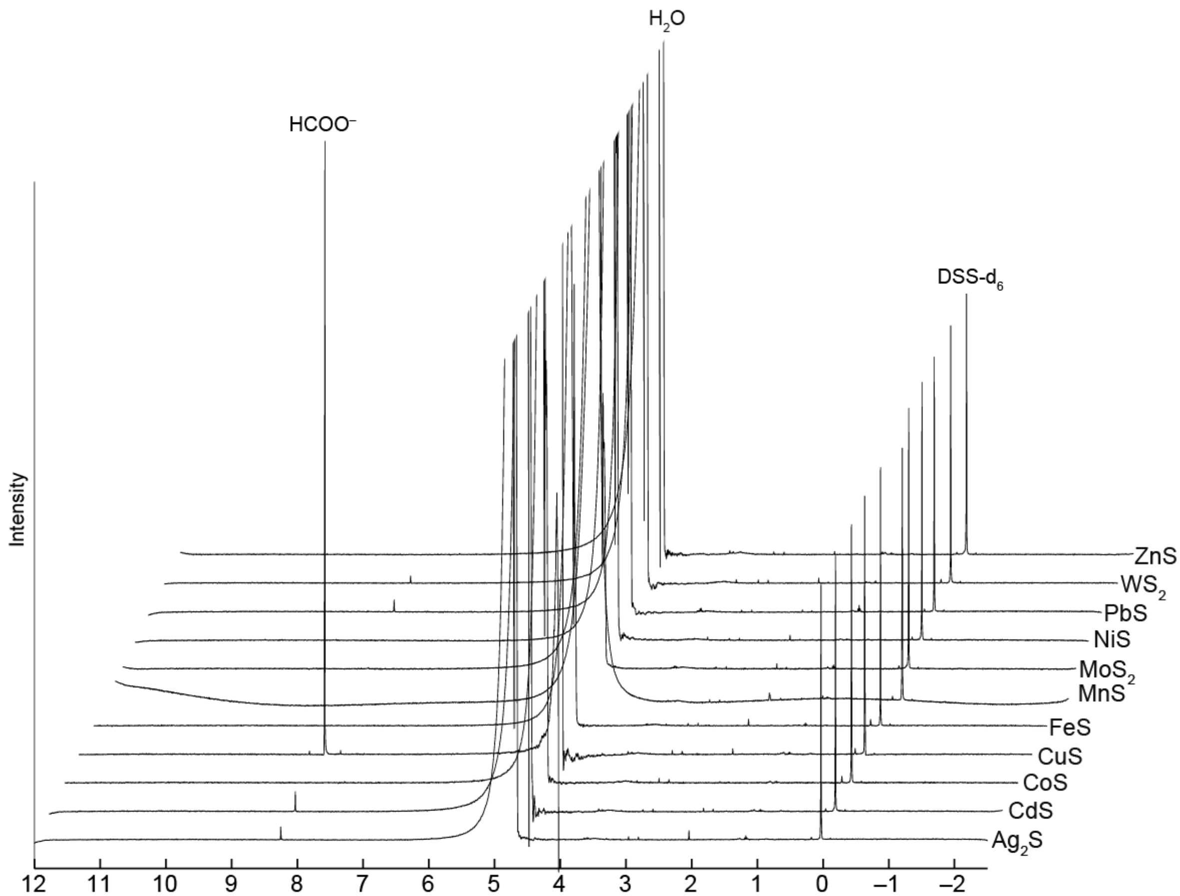

fig. S4. [1]H NMR spectra of the CO_2-saturated 0.1 M NaCl after applying –1.2 V (versus SHE) for 24 hours in the presence of metal sulfides.

table S1. Summary of total current densities and FEs for CO_2 reduction on metal sulfides.

sulfide	E [vs. SHE]	j [mA cm^{-2}]	$HCOO^-$ [%]	CO [%]
Ag_2S	–0.6	0.20	0.0	0.0
	–0.7	0.55	0.0	0.0
	–0.8	1.32	0.0	0.0
	–0.9	1.02	0.1	3.0
	–0.95	1.26	0.1	2.9
	–1.0	1.30	0.2	13.5
	–1.1	1.81	0.5	29.1
	–1.2	1.33	0.5	25.2
CdS	–0.6	0.01	0.0	0.0
	–0.7	0.08	0.0	0.1
	–0.8	0.10	0.1	0.4
	–0.9	0.19	0.4	4.2
	–0.95	0.22	0.5	15.3
	–1.0	0.39	1.4	42.5
	–1.1	0.39	1.4	33.5
	–1.2	0.46	1.6	42.1
CoS	–0.8	0.86	0.1	0.1
	–1.0	2.61	0.1	0.0
	–1.2	8.86	0.0	0.0
CuS	–0.8	0.97	0.3	0.0
	–1.0	4.04	3.7	0.0
	–1.2	4.75	4.7	0.0
FeS	–0.8	0.96	0.1	0.1
	–1.0	3.08	0.0	0.0
	–1.2	9.60	0.0	0.0
MnS	–0.8	0.02	0.0	0.1
	–1.0	0.13	0.0	0.0
	–1.2	0.11	0.0	0.0
MoS_2	–0.8	0.26	0.6	0.0
	–1.0	1.77	0.2	0.0
	–1.2	3.15	0.0	0.0
NiS	–0.8	1.26	0.2	0.0
	–1.0	3.12	0.0	0.0
	–1.2	5.88	0.0	0.0
PbS	–0.8	0.25	0.0	0.0
	–1.0	0.81	0.0	0.1
	–1.2	2.51	0.3	0.0
WS_2	–0.8	0.73	0.6	0.0
	–1.0	1.63	0.3	0.1
	–1.2	6.09	0.1	0.0
ZnS	–0.8	0.02	0.0	0.0
	–1.0	0.02	0.0	0.1
	–1.2	0.84	0.0	0.0

table S2. Peak list of x-ray diffraction patterns of metal sulfides.

Sulfide	2θ [º]	Rel. Int.	Assignment
Ag_2S	22.4	9.4	Acanthite
	24.9	3.0	Acanthite
	25.9	32.2	Acanthite
	26.3	23.4	Acanthite
	27.8	3.4	Halite
	28.9	63.8	Acanthite
	31.5	89.7	Acanthite
	32.2	7.2	Halite
	33.6	47.7	Acanthite
	34.4	100.0*	Acanthite
	34.7	72.1	Acanthite
	36.5	45.9	Acanthite
	36.8	76.7	Acanthite
	37.1	49.1	Acanthite
	37.7	93.8	Acanthite
	40.7	49.9	Acanthite
	43.4	38.8	Acanthite
	43.6	14.4	Acanthite
	44.2	16.0	Acanthite
	45.4	13.9	Acanthite
	45.7	3.1	Acanthite
	46.2	28.3	Acanthite
	47.4	3.4	Acanthite
	47.7	14.9	Acanthite
	48.7	11.9	Acanthite
	50.7	1.9	Acanthite
	51.1	1.9	Acanthite
	52.8	7.1	Acanthite
	53.3	23.3	Acanthite
	54.2	4.6	Acanthite
	54.8	1.7	Acanthite
	57.2	1.7	Acanthite
	58.1	6.7	Acanthite
	58.4	9.7	Acanthite
	59.4	4.8	Acanthite
	59.7	3.3	Acanthite
	60.0	7.2	Acanthite
	61.1	7.7	Acanthite
	62.6	6.8	Acanthite
	63.2	5.3	Acanthite
	63.7	16.1	Acanthite
	64.3	2.3	Acanthite
	65.8	2.1	Acanthite
	69.8	6.4	Acanthite
	70.4	3.2	Acanthite
	70.6	6.1	Acanthite
	71.4	2.5	Acanthite
	72.3	5.0	Acanthite
	74.8	1.6	Acanthite

Sulfide	2θ [º]	Rel. Int.	Assignment
Ag_2S	86.3	2.4	Acanthite
	89.5	1.5	Acanthite
CdS	26.7	100.0*	Hawleyite
	43.9	31.6	Hawleyite
	51.9	27.3	Hawleyite
	71.3	5.4	Hawleyite
	80.5	1.7	Hawleyite
CoS	30.0	–	Cobaltpentlandite
	52.6	100.0*	Cobaltpentlandite
CuS	27.7	28.0	Covellite
	29.4	57.4	Covellite
	31.8	22.3	Covellite
	32.4	59.6	Covellite
	48.0	100.0	Covellite
	52.7	12.4	Covellite
	59.3	28.5	Covellite
FeS	17.3	100.0*	Mackinawite
	30.4	–	Mackinawite
	39.0	–	Mackinawite
	49.7	–	Mackinawite
MnS	25.9	100*	Rambergite
	27.8	99.9	Rambergite
	29.5	64.4	Rambergite
	38.4	14.5	Rambergite
	45.7	83.6	Rambergite
	50.2	40.2	Rambergite
	54.3	42.1	Rambergite
	55.1	7.7	Rambergite
	79.5	7.6	Rambergite
MoS_2	14.2	100*	Molybdenite
	28.9	1.8	Molybdenite
	32.5	1.0	Molybdenite
	33.4	0.5	Molybdenite
	35.7	0.5	Molybdenite
	39.4	3.8	Molybdenite
	44.0	6.4	Molybdenite
	49.6	3.1	Molybdenite
	55.9	0.4	Molybdenite
	58.2	0.6	Molybdenite
	60.0	4.9	Molybdenite
	62.7	0.3	Molybdenite
	70.0	0.7	Molybdenite
	72.6	0.3	Molybdenite
	75.9	0.2	Molybdenite
	77.5	0.5	Molybdenite
	78.1	0.2	Molybdenite
	80.1	0.2	Molybdenite
	86.6	0.1	Molybdenite
	88.6	0.5	Molybdenite

Sulfide	2θ [º]	Rel. Int.	Assignment
NiS	30.1	72.4	NiS
	31.7	12.8	Halite
	34.6	57.0	NiS
	37.3	6.5	?
	43.3	6.5	?
	45.7	100.0*	NiS
	53.5	51.7	NiS
	70.5	3.8	NiS
	73.1	13.5	Halite
PbS	25.9	80.6	Galena
	30.0	100.0*	Galena
	43.0	75.0	Galena
	50.9	47.2	Galena
	53.3	24.7	Galena
	62.4	10.9	Galena
	68.7	14.7	Galena
	70.8	26.1	Galena

Sulfide	2θ [º]	Rel. Int.	Assignment
PbS	78.8	16.3	Galena
	84.8	8.5	Galena
WS_2	14.2	100*	Tungstenite
	24.1	4.1	?
	28.5	6.3	Tungstenite
	33.3	57.5	Tungstenite
	39.9	20.8	Tungstenite
	43.4	4.4	Tungstenite
	49.3	6.3	Tungstenite
	58.7	24.9	Tungstenite
	60.4	15.7	Tungstenite
	69.1	6.9	Tungstenite
	73.2	2.3	Tungstenite
ZnS	29.1	100.0*	Sphalerite
	48.0	34.5	Sphalerite
	56.6	23.1	Sphalerite
	78.7	3.3	Sphalerite

Continued.